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Heterogeneity in Polymer Thin Films

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Abstract. In the last two decades very extensive studies have been performed on polymer thin films to reveal very interesting but unusual properties. One of the most interesting findings is the decrease in glass transition temperature T_g with film thickness in polystyrene (PS) thin film supported on Si substrate. Another interesting finding is apparent negative thermal expansivity in glassy state for thin films below ~ 25 nm. In order to understand the unusual properties of polymer thin films we have studied temperature dependence of thickness of polystyrene thin films by means of X-ray and neutron reflectivity. In addition, we also studied dynamics of PS thin films using inelastic neutron scattering. In the presentation we will discuss the results from viewpoints of heterogeneity of polymer thin films. Finally we did neutron reflectivity measurements on a 5-layer thin film, consisting of alternatively stacked d-PS and h-PS layers to see the distribution of glass transition temperature and thermal expansivity directly.

Keywords: Polymer thin film, glass transition, X-ray reflectivity, Neutron reflectivity, Inelastic neutron reflectivity, heterogeneity.

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INTRODUCTION

Recent extensive studies on polymer thin films have revealed very interesting but unusual properties of polymer thin films. Glass transition of thin films is one of the most interesting topics in the field because many properties such as mechanical and thermal properties change drastically at the glass transition temperature T_g . In a pioneering work by Keddie et al. [1] it was reported that the glass transition temperature of polystyrene thin films supported on silicon substrate decreases with decreasing thickness below ~ 40 nm. Similar results were reported by many researchers on T_g of polystyrene thin films supported on silicon substrate. On the other hand, T_g increases with decreasing the film thickness for poly(methyl methacrylate)(PMMA) supported on silicon substrate [2], suggesting strong interactions between them. Thus, surface and/or interfacial effects seem to play an important role on glass transition. In order to reveal the cause of the decrease in T_g Kajiyama et al. [3-5] have studied T_g of the surface layer of polystyrene thin films to find a lower glass transition temperature T_g , and concluded that as the film thickness decreases the fraction of the surface layer increases, resulting in the reduction in T_g . This is very normal explanation for the reduction in T_g for thin films. Another interesting finding is the reduction of thermal expansivity with film thickness, which was first reported by NIST

group [6]. It was revealed that one of the causes of the reduction was structure relaxation during the heating due to lack of annealing. However, the annealing experiments on thin films thickness [7] showed that the thermal expansivity decreased with film thickness even after long annealing above T_g . This could be interpreted in terms of hard layer near the substrate, suggesting heterogeneous structure of polymer thin films.

It should be noted that polymers have wide distribution of the relaxation time in time scale as well as in length scale. Therefore, in order to understand the unusual properties of thin films we have to reveal the distribution of T_g as well as the dynamic nature. In other words, revealing heterogeneous structure and/or dynamics in polymer thin films is essential to understand the unusual properties. This has been already pointed out by de Gennes [8], and he mentioned that further experiments should not aim at the determination of a single T_g , but at a distribution of T_g 's. Recent works by Torkelson et al. [9] along the direction are remarkable. Using a fluorescence technique they examined glass transition temperature at surface, interface and in between of multilayer films.

In this report we studied the dynamics of polymer thin films by inelastic neutron scattering, and the distribution of glass transition temperature T_g in a multi-layer polystyrene thin film by neutron

reflectivity, aiming to elucidate the heterogeneous structure or multi-layer structure of polymer thin films.

EXPERIMENTAL

The sample used for the inelastic scattering experiments was PS with molecular weight $M_w = 2.90 \times 10^5$ and molecular weight distribution $M_w/M_n = 1.06$. Thin films were prepared by spin-coating toluene solutions of PS at 2000 rpm on flat glass plates rinsed in toluene prior to spin-coating. The film was removed from the glass plate onto water surface and then collected on Al foil 15 mm thick, and then annealed at 413 K for 12 h after drying in vacuum at room temperature for 2 days. We used 300 sheets for both 1000 and 200 Å films. For neutron reflectivity (NR) measurements we used deuterated polystyrene (d-PS) and hydrogenated polystyrene (h-PS) with molecular weight $M_w = 7.31 \times 10^5$ and $M_w = 7.69 \times 10^5$, and molecular weight distributions were $M_w/M_n = 1.18$ and 1.08, respectively. The sample was annealed at 408 K for 5 min after drying in vacuum at 343 K for 2 days.

Inelastic neutron scattering measurements were performed with two spectrometers. One is an inverted geometry time of flight (TOF) spectrometer LAM-40 with an energy resolution of ~ 0.2 meV, KEK, Tsukuba. Another is a direct geometry spectrometer MARI with an energy resolution 0.34 meV at ISIS, Rutherford Appleton Laboratory, Didcot.

Neutron reflectivity (NR) measurements were performed using MINE spectrometer at JRR-3 reactor in Tokai, and ARISA-II at BL16 in J-PARC in Tokai.

RESULTS AND DISCUSSION

Inelastic neutron scattering measurements on the PS thin films were done in a temperature range below and above the glass transition temperature T_g . First we have evaluated the mean square displacement $\langle u^2 \rangle$ from the Q dependence of the elastic scattering intensity. The evaluated $\langle u^2 \rangle$ at 230 K is shown in Fig. 1 as a function of film thickness. It is clear that the $\langle u^2 \rangle$ decreases with film thickness. Analyzing the inelastic scattering part of the spectra for the thin films we also found that the density of phonon states $G(\omega)$ decreases with the film thickness according to the reduction in $\langle u^2 \rangle$. Both of the findings suggest that some hardening occurred in the thin film. We considered two possibilities for the decrease in $\langle u^2 \rangle$ or the hardening with film thickness. One is the hardening of polymer chains due to the spatial confinement (confinement effect). Another possibility is that a hard layer (lower mobility layer) would exist at the interface between the polymer thin film and the

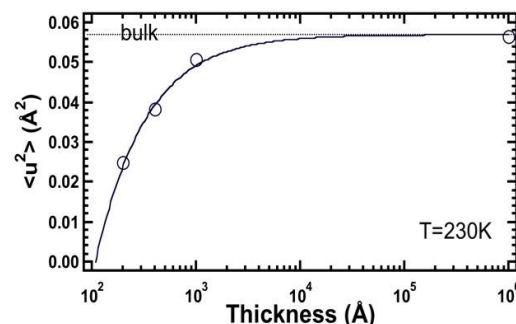


Fig. 1 Mean square displacement $\langle u^2 \rangle$ of PS thin films at 230 K as a function of film thickness.

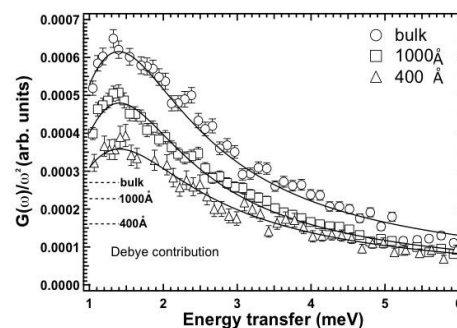


Fig. 2. Density of phonon states $G(\omega)$ for PS bulk, thin films 1000 Å and 400 Å thick. Dashed lines show the Debye contribution.

substrate. In order to see which cause is more plausible, we prepared thin films 40 nm thick for different molecular weights (M_w), giving different ratios of the film thickness ($=d$) to the double radius of gyration ($2R_g$). If the confinement effect were dominant, the decrease of $\langle u^2 \rangle$ would be observed with the decrease of ratio of $d/2R_g$ because decreasing the ratio $d/2R_g$ means an increase of spatial confinement. And if the interface effect were dominant, $\langle u^2 \rangle$ would be constant regardless of the ratio $d/2R_g$ because the ratio is constant under the same film thickness. We found [10] that $\langle u^2 \rangle$ was independent of molecular weight, at least, within the experimental error. We therefore concluded that the decrease in $\langle u^2 \rangle$ is caused due to the hard layer near the substrate, suggesting heterogeneous structure in the thin films.

We also studied the non-Gaussian parameter A_0 of polymer thin films to study the dynamic heterogeneity [11]. We found that the non-Gaussian parameter A_0 increased with decreasing the film thickness (Fig. 3), showing the dynamic heterogeneity increased with decreasing the film thickness, again suggesting that the polymer thin films have heterogeneous structure.

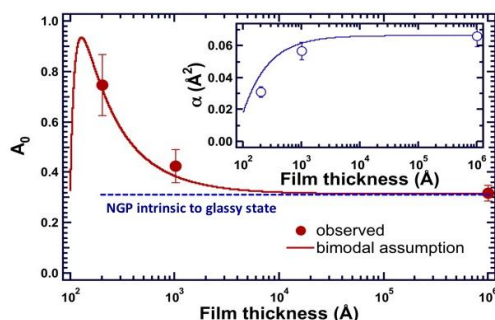


Fig. 3. Non-Gaussian parameter as a function of film thickness at 230 K. Inset shows the mean square displacement for PS thin films.

Next we performed neutron reflectivity measurements on a 5-layer thin film, consisting of alternatively stacked d-PS and h-PS layers (see Fig. 4). Each layer is ~ 20 nm thick and the total thickness is ~ 100 nm. We have analyzed the reflectivity profiles to evaluate thickness of each layer and interface and surface roughness as a function of temperature. The temperature dependence of the total film thickness is shown at top in Fig. 5. The total film thickness increases with temperature in the glassy state up to ~ 372 K and begins to increase more steeply above ~ 372 K, showing the glass transition temperature T_g is ~ 372 K, which is almost the same as the bulk glass transition temperature. It is noted that in

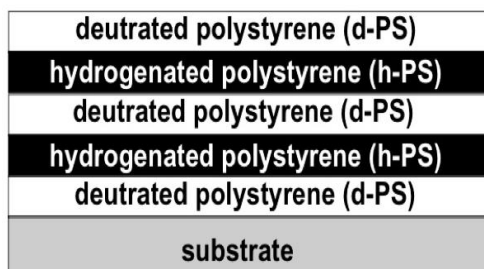


Fig. 4 Schematic representation of 5-layer thin film consisting of alternatively stacked d-PS and h-PS layers.

this thin film we did not observe the decrease in thickness slightly below T_g , which was typically observed in not-well annealed thin films [7] and assigned to structure relaxation due to lack of annealing. The present observation suggests that the annealing condition in this experiment is enough to avoid the structure relaxation near T_g . The temperature dependences of the thickness for the 1st, 2nd, 3rd, 4th and more steeply, showing that the glass transition temperature of the surface layer is ~ 20 K lower than

5th layer from top (surface) to bottom are shown in Fig. 5. The surface layer increases in thickness with temperature, while it begins to increase above ~ 356 K

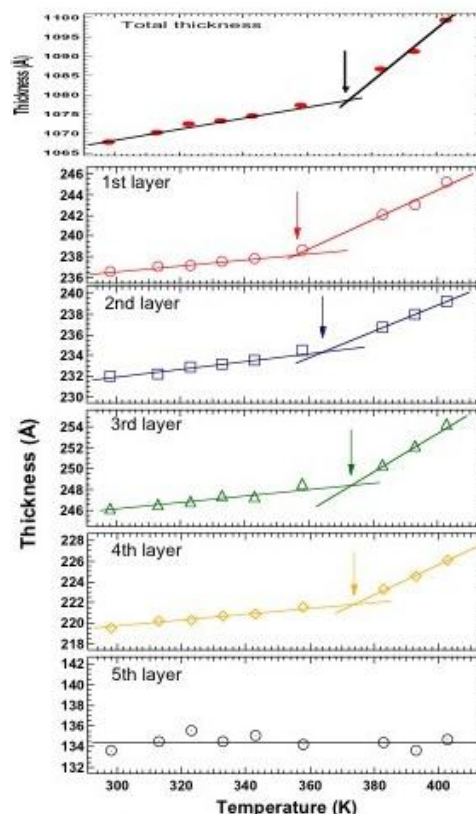


Fig. 5 Temperature dependence of film thickness of each layer.

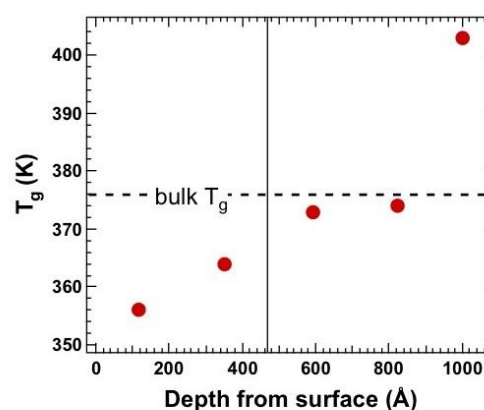


Fig. 6 Distribution of glass transition temperature T_g in 5-layer thin film

the bulk T_g . The glass transition temperature T_g increases with departing from the surface. The T_g 's of the 3rd and 4th layers are almost the same as that of bulk. On the other hand, the bottom layer (5th layer)

shows very different temperature dependence of the thickness from other layers. The film thickness is almost independent of temperature below 403K. In the temperature range examined we did not observe the increase in thickness, suggesting that the glass transition temperature of the bottom layer must be higher than 403K. The present results clearly show that the thin film has a distribution of T_g (Fig. 6) even though the T_g of the total thickness is the same as the bulk T_g .

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